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Crystal and Molecular Structure of Dichlorobis(2,2'-bis-(dimethylarsino)biphenyl)-nickel(II)

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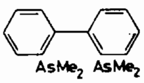
The crystal structure of dichlorobis(2,2'-bis-(dimethylarsino)biphenyl)nickel(II) has been determined from single-crystal X-ray diffraction data collected on a two-circle diffractometer. The analysis was carried out on 2542 reflections and refined by full-matrix least-squares calculations to a final R of 0.042. The crystals are triclinic, space group $P\bar{1}$ with a = *15.289(6),* b = *11.241(5),* c = *10.336(5) Å,* α = *87.55(4),* β = *99.75(5),* γ = *102.57(6)° and* Z = *2. The complex is monomeric with nickel in a distorted* trans-*octahedral environment of four arsenic and two chlorine atoms.*

Introduction

While the co-ordination chemistry of *o*-phenylenebis(dimethylarsine) (*pdma*) and 1,8-bis(dimethylarsino)naphthalene with metal ions is well documented [1–3], only recently has the related 2,2'-bis(dimethylarsino)biphenyl (1, *dmab*) been studied [4]. Reactions of *dmab* with nickel(II) halides or thiocyanate give green crystalline complexes [4] of composition $[NiX_2(dmab)_2]$ (X = Cl, Br, I or NCS). Solid-state (diffuse reflectance) electronic spectra and magnetic moment data are consistent with a pseudo-octahedral chelate structure, although the possibility of a polymeric structure with bridging diarsine ligands cannot be ruled out. Pseudo-octahedral complexes of nickel(II) with diarsines are rare and crystallographic studies appear to be limited to the *trans*-octahedral $[NiI_2(pdma)_2]$, [5]. It is interesting to note that while the Ni–I distances (3.215(2) Å) in the latter complex are considered to be significantly less than for an electrostatic interaction, the complex is nevertheless brown in colour and diamagnetic [6, 7]. In contrast, the above *dmab* complexes are paramagnetic and it is to establish the nature of the coordination geometry for these compounds that the first crystal structure of a *dmab* metal complex, $[NiCl_2(dmab)_2]$, has been determined.



(1)

Experimental

$[NiCl_2(dmab)_2]$ was prepared as previously described [4] to give green needles suitable for crystal X-ray analysis.

Crystal Data

$NiC_{32}H_{40}Cl_2As_4$, M_r = 853.98. Triclinic $P\bar{1}$, a = 15.289(6), b = 11.241(5), c = 10.336(5) Å, α = 87.55(4), β = 99.75(5), γ = 102.57(6)°, U = 1708.7 Å^3, D_m (by flotation) = 1.68, D_c = 1.66 g cm^{-3}. Z = 2, Mo-Kα, λ = 0.7107 Å, μ(Mo-Kα) = 44.5 cm^{-1}, $F(000)$ = 852.

Intensity Measurements

A crystal of dimensions 0.10 × 0.15 × 0.35 mm was mounted with the *c*-axis coincident with the rotation (ω) axis of a Stöe Stadi 2 two-circle diffractometer. Using monochromated Mo-Kα radiation and the background–ω scan–background technique, 4458 unique reflections were measured, of which 2542 had $I > 3\sigma(I)$ and were considered to be observed [the net intensity $I = T - B$, where T = scan count, B = mean background count over the scan width; $\sigma(I) = (T + Bc/2t)^{1/2}$, where c = scan time, t = time for background measurements at each end of the scan]. Corrections for Lorentz, polarization and absorption effects were made.

Structure Determination and Refinement

The nickel and arsenic atom positions were determined from the three-dimensional Patterson function and the remaining atoms were located from succes-

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TABLE I. Final Atomic Parameters. Estimated Standard Deviations for Non-Hydrogen Atoms are Given in Parentheses.

(a) *Fractional Co-ordinates* ($\times 10^4$)

	x	y	z
Ni	2406(1)	2278(1)	7397(1)
As1	2125(1)	–2(1)	7377(1)
As2	3619(1)	2221(1)	6067(1)
As3	1036(1)	2372(1)	8380(1)
As4	2908(1)	4529(1)	7848(1)
Cl(1)	1479(2)	2453(3)	5339(3)
Cl(2)	3336(2)	2100(2)	9465(3)
C1	1617(8)	–758(11)	8909(11)
C2	1320(7)	–1002(10)	598(11)
C3	4840(7)	2129(11)	6877(13)
C4	3902(9)	3591(10)	4877(12)
C5	1018(9)	2319(12)	10316(11)
C6	–53(8)	1135(11)	7776(15)
C7	4231(7)	5094(11)	8179(12)
C8	2591(8)	5806(11)	6646(12)
C11	3244(6)	–612(9)	7574(10)
C12	3645(8)	–931(10)	8838(11)
C13	4438(8)	–1342(11)	8992(12)
C14	4888(8)	–1435(10)	7954(13)
C15	4512(7)	–1083(10)	6714(12)
C16	3692(7)	–683(9)	6513(10)
C21	3284(7)	893(10)	4803(10)
C22	2923(8)	1145(10)	3490(10)
C23	2695(9)	250(14)	2583(12)
C24	2783(8)	–939(12)	2869(12)
C25	3106(8)	–1204(11)	4169(12)
C26	3354(7)	–317(10)	5121(10)
C31	604(7)	3852(10)	7867(10)
C32	–78(8)	3816(11)	6773(12)
C33	–444(8)	4836(15)	6366(12)
C34	–99(9)	5893(13)	7026(15)
C35	606(8)	5990(11)	8094(13)
C36	974(7)	4967(10)	8500(11)
C41	2592(6)	4960(9)	9497(10)
C42	3264(7)	5095(11)	10644(12)
C43	3101(9)	5407(13)	11804(13)
C44	2260(10)	5630(13)	11918(14)
C45	1590(8)	5501(12)	10866(13)
C46	1741(7)	5151(10)	9608(12)
H101	1997	–296	9790
H102	1659	–1706	8970
H103	915	–690	8811
H201	1514	–695	5046
H202	628	–925	5983
H203	1372	–1942	6142
H301	4812	1395	7588
H302	5172	2979	7362
H303	5216	1963	6133
H401	3279	3775	4327
H402	4314	3370	4208
H403	4270	4387	5437
H501	300	1989	10316
H502	1398	1867	11086
H503	1180	2130	9379
H601	84	239	7997
H602	–241	1232	6728

(continued on facing page)

TABLE I. *(continued)*

H603	–602	1251	8258
H701	4528	4466	8843
H702	4405	5989	8614
H703	4491	5135	7265
H801	1863	5631	6357
H802	2908	5822	5785
H803	2823	6675	7134
H12	3329	–852	9680
H13	4725	–1603	9962
H14	5509	–1769	8103
H15	4855	–1120	5890
H22	2828	2051	3215
H23	2431	472	1587
H24	2608	–1629	2118
H25	3168	–2126	4432
H32	–322	2985	6214
H33	–1000	4772	5556
H34	–363	6690	6699
H35	860	6839	8619
H42	3563	4839	9851
H43	3627	5459	12654
H44	2149	5925	12847
H45	955	5474	10212

(b) *Anisotropic Thermal Parameters* ($\times 10^4$) *of the Form:*

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	315(7)	384(8)	344(8)	101(6)	7(6)	18(6)
As1	400(6)	388(7)	338(6)	78(5)	30(5)	–1(5)
As2	421(7)	412(7)	415(7)	77(5)	99(6)	28(5)
As3	299(6)	408(7)	439(7)	77(5)	45(5)	8(6)
As4	311(6)	377(7)	418(7)	61(5)	10(5)	20(5)
Cl(1)	548(19)	773(22)	418(17)	305(17)	–67(15)	27(16)
Cl(2)	484(17)	513(18)	387(16)	173(14)	–74(14)	39(14)
C1	608(79)	621(81)	486(76)	–22(64)	147(64)	65(64)
C2	341(63)	681(81)	486(72)	–19(56)	2(56)	–150(63)
C3	360(67)	736(90)	943(102)	152(62)	–17(68)	–216(78
C4	950(104	488(79)	728(91)	–107(72)	501(82)	–15(68)
C5	860(98)	1102(112)	301(76)	357(84)	257(71)	194(73)
C6	564(85)	515(85)	1093(121)	–50(67)	14(84)	–21(83)
C7	327(64)	615(83)	625(86)	33(58)	126(61)	–54(69)
C8	664(86)	614(87)	544(84)	165(69)	–36(71)	200(70)
C11	365(62)	439(67)	355(64)	153(52)	–31(53)	–7(52)
C12	642(81)	537(77)	424(72)	213(64)	37(63)	–3(59)
C13	686(91)	701(90)	488(81)	364(74)	–110(73)	90(69)
C14	449(73)	469(77)	769(96)	98(60)	–160(73)	73(70)
C15	442(70)	552(77)	618(82)	217(60)	–4(63)	19(64)
C16	335(61)	451(68)	461(71)	175(52)	–83(55)	–98(56)
C21	411(64)	563(75)	337(65)	165(55)	80(53)	–92(55)
C22	723(84)	553(77)	244(63)	208(64)	48(59)	81(58)
C23	748(98)	930(116)	400(78)	90(85)	5(70)	–156(83)
C24	654(90)	713(97)	463(84)	44(73)	–140(69)	–132(72)
C25	587(81)	525(80)	627(87)	182(64)	37(69)	–162(70)
C26	389(62)	443(69)	387(65)	212(53)	87(52)	16(56)
C31	283(62)	609(84)	297(62)	149(58)	22(53)	–18(58)
C32	503(75)	690(90)	479(80)	272(68)	11(66)	–102(69)
C33	473(77)	1211(131)	346(73)	424(90)	122(62)	186(83)
C34	487(76)	826(102)	811(108)	426(78)	221(81)	399(88)

(continued overleaf)

TABLE I. *(continued)*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C35	446(71)	468(77)	785(99)	155(61)	79(73)	35(71)
C36	293(60)	422(72)	508(73)	76(54)	84(55)	92(60)
C41	207(52)	372(64)	397(64)	36(45)	42(49)	–26(51)
C42	386(69)	571(83)	541(81)	–64(59)	81(65)	–27(65)
C43	440(79)	1103(119)	478(91)	–73(74)	50(69)	–83(82)
C44	641(115)	1138(126)	577(95)	–145(94)	164(89)	–365(87)
C45	459(75)	714(103)	629(89)	–86(68)	135(69)	–165(77)
C46	351(69)	484(78)	493(80)	53(58)	20(62)	79(63)

TABLE II. Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

Symmetry Code

none	x, y, z
(i)	$-x, 1.0 - y, 1.0 - z$
(ii)	$1.0 - x, -y, 2.0 - z$

Bond Lengths

Ni–As1	2.505(2)	C14–C15	1.392(17)
Ni–As2	2.501(2)	C15–C16	1.402(16)
Ni–As3	2.502(2)	C16–C26	1.515(14)
Ni–As4	2.519(2)	C21–C26	1.408(16)
Ni–Cl(1)	2.374(3)	C21–C22	1.417(14)
Ni–Cl(2)	2.384(3)	C22–C23	1.353(18)
As1–C1	1.961(12)	C23–C24	1.386(21)
As1–C2	1.948(10)	C24–C25	1.394(17)
As1–C11	1.955(11)	C25–C26	1.378(16)
As2–C3	1.934(11)	C31–C32	1.397(14)
As2–C4	1.950(12)	C31–C36	1.399(15)
As2–C21	1.951(11)	C32–C33	1.401(21)
As3–C5	2.004(12)	C33–C34	1.352(21)
As3–C6	1.952(11)	C34–C35	1.395(17)
As3–C31	1.941(12)	C35–C36	1.406(17)
As4–C7	1.960(10)	C36–C46	1.480(14)
As4–C8	1.945(13)	C41–C42	1.422(14)
As4–C41	1.956(11)	C41–C46	1.388(16)
C11–C12	1.413(15)	C42–C43	1.341(20)
C11–C16	1.402(16)	C43–C44	1.388(22)
C12–C13	1.371(19)	C44–C45	1.351(18)
C13–C14	1.388(20)	C45–C46	1.443(19)
As1. .As2	3.402	Cl(1). . H34^{i}	2.758
As3. .As4	3.431	Cl(2). .H14^{ii}	2.877

Bond Angles (°)

As1–Ni–As2	85.6(1)	As1–C11–C16	122.2(7)
As1–Ni–As3	95.4(1)	C12–C11–C16	118.6(10)
As1–Ni–As4	168.2(1)	C11–C12–C13	119.7(11)
As1–Ni–Cl(1)	95.3(1)	C12–C13–C14	122.8(11)
As1–Ni–Cl(2)	84.6(1)	C13–C14–C15	117.7(12)
As2–Ni–As3	170.8(1)	C14–C15–C16	121.1(12)
As2–Ni–As4	94.6(1)	C11–C16–C15	120.0(10)
As2–Ni–Cl(1)	85.0(1)	C11–C16–C26	123.7(10)

Table II. *(continued)*

As2–Ni–Cl(2)	95.0(1)	C15–C16–C26	116.2(10)
As3–Ni–As4	86.2(1)	C16–C26–C21	121.2(9)
As3–Ni–Cl(1)	85.8(1)	C16–C26–C25	118.3(10)
As3–Ni–Cl(2)	94.2(1)	C21–C26–C25	120.5(10)
As4–Ni–Cl(1)	96.4(1)	As2–C21–C22	118.4(8)
As4–Ni–Cl(2)	83.6(1)	As2–C21–C26	124.0(7)
Cl(1)–Ni–Cl(2)	179.9(1)	C22–C21–C26	117.5(10)
Ni–As1–Cl	112.9(4)	C21–C22–C23	120.0(11)
Ni–As1–C2	123.6(3)	C22–C23–C24	123.3(11)
Ni–As1–C11	112.9(4)	C23–C24–C25	117.0(12)
C1–As1–C2	100.2(4)	C24–C25–C26	121.6(11)
C1–As1–C11	100.6(5)	As3–C31–C32	118.5(9)
C2–As1–C11	103.7(5)	As3–C31–C36	123.1(7)
Ni–As2–C3	122.0(4)	C32–C31–C36	118.3(11)
Ni–As2–C4	116.5(4)	C31–C32–C33	121.8(11)
Ni–As2–C21	113.2(4)	C32–C33–C34	118.6(11)
C3–As2–C4	99.3(5)	C33–C34–C35	121.9(14)
C3–As2–C21	103.2(5)	C34–C35–C36	119.5(11)
C4–As2–C21	99.4(5)	C31–C36–C35	119.7(9)
Ni–As3–C5	123.7(4)	C31–C36–C46	123.9(10)
Ni–As3–C6	115.6(5)	C35–C36–C46	116.4(10)
Ni–As3–C31	111.6(3)	C36–C46–C41	122.5(11)
C5–As3–C6	100.4(6)	C36–C46–C45	118.8(10)
C5–As3–C31	101.5(5)	C41–C46–C45	118.7(10)
C6–As3–C31	100.8(5)	As4–C41–C42	118.8(8)
Ni–As4–C7	113.2(4)	As4–C41–C46	123.3(7)
Ni–As4–C8	124.9(3)	C42–C41–C46	117.8(10)
Ni–As4–C41	112.0(3)	C41–C42–C43	122.2(11)
C7–As4–C8	99.3(5)	C42–C43–C44	120.4(12)
C7–As4–C41	101.1(4)	C43–C44–C45	120.1(14)
C8–As4–C41	103.2(5)	C44–C45–C46	120.7(13)
As1–C11–C12	119.1(9)		

sive difference electron-density maps. Hydrogen atoms were included in positions calculated from the geometry of the molecule (C–H = 1.08 Å). Common isotropic temperature factors were applied to methyl and phenyl hydrogens and refined to final values of U = 0.127(17) and 0.107(17) Å^2 respectively. Scattering factors were calculated [8] using an analytical approximation and the weighting scheme adopted

TABLE III. Equations of Least-Squares Planes Referred to the Orthogonal Axis System *a*, *b*′, *c** with Distances (Å) of Relevant Atoms from the Planes in Square Brackets.

Plane A: C11–C16

$-0.2972X - 0.9412Y - 0.1608Z + 1.7889 = 0.0000$

[C11, 0.011; C12, −0.013; C13, 0.003; C14, 0.010; C15, −0.012; C16, 0.001; As1, −0.043; C26, −0.033]

Plane B: C21–C26

$0.9538X + 0.2153Y - 0.2096Z - 2.9544 = 0.0000$

[C21, 0.016; C22, −0.012; C23, −0.003; C24, 0.014; C25, −0.009; C26, −0.006; As2, 0.029; C16, −0.042]

Plane C: C31–C36

$0.7475X + 0.2497Y - 0.6155Z + 4.8812 = 0.0000$

[C31, −0.027; C32, 0.018; C33, 0.000; C34, −0.008; C35, −0.002; C36, 0.019; As3, −0.056; C46, 0.074]

Plane D: C41–C46

$0.1407X + 0.9630Y - 0.2300Z - 3.2173 = 0.0000$

[C41, 0.008; C42, 0.001; C43, −0.009; C44, 0.009; C45, −0.001; C46, −0.008; As4, 0.053; C36, −0.081]

Plane E: As1, As2, Ad3, As4

$-0.4678X + 0.0857Y - 0.8797Z + 7.2928 = 0.0000$

[As1, −0.230; As2, 0.231; As3, 0.228; As4, −0.229; Ni, 0.028; C16, −0.790; C26, 0.661; C36, 0.715; C46, −0.696]

Angles Between Planes (°)

A/B	63.1	C/D	60.8
A/E	78.5	C/E	77.7
B/E	75.9	D/E	77.4

was $w = 0.9580/[\sigma^2(F_o) + 0.0007\,(F_o)^2]$. Full matrix refinement with anisotropic temperature factors for all non-hydrogen atoms gave the final $R = 0.042$ and $R' = 0.041$. The final difference-Fourier map showed no peaks greater than 0.60 $e\text{Å}^{-3}$. Final atomic parameters are listed in Table I, bond distances and angles in Table II. A list of observed and calculated structure factors is available from the Editor.

Calculations

All calculations, apart from preliminary data processing, were carried out on an IBM 370/165 computer at the SRC Computing Centre, Daresbury, using the SHELX computing package [9].

Results and Discussion

The complex is found to be monomeric with the nickel surrounded by a distorted *trans*-octahedral arrangement of four arsenic and two chlorine atoms (Fig. 1). The molecule has approximate C_2 symmetry with the two-fold rotation axis lying along the direction of the Ni–Cl bonds. The arsenic atoms are not coplanar but lie at distances ranging from +0.231 to −0.230 Å out of the best least-squares plane (Table III), such that the As1–Ni–As4, As2–Ni–As3 groupings are non-linear (bond angles 168.2, 170.8(1)° respectively). These distortions relieve crowding between the chlorine atoms and the methyl groups and are accompanied by angular distortion of the methyl groups about arsenic. Thus for each of the four arsenic atoms one Ni–As–CH_3 angle is significantly greater (mean 123.6°) than the regular tetrahedral value, while the H_3C–As–CH_3 angle is reduced to about 100°. The resulting Cl. . . .C-(methyl) distances of 3.63–3.97 Å are longer than the values (3.50–3.56 Å) found [10] in [$NiCl_2$(*pdma*)$_2$]Cl.

The two chlorine atoms lie at distances of 2.374(3) and 2.384(3) Å from nickel and are arranged such that the Cl–Ni–Cl grouping is effectively linear (179.9(1)°). The Ni–Cl bond distances are significantly shorter than the value of 2.425(3) Å found in the nickel(III) complex [$NiCl_2$(*pdma*)$_2$]Cl, [10]. The length of the Ni–Cl bonds in the latter complex cation has been attributed to the antibonding effects of the unpaired electron in the nickel d_{z^2} orbital which is directed along the direction of the Ni–Cl bonds. It is difficult to ascertain the importance of such antibonding effects upon the Ni–Cl bond strength in the present complex for the two

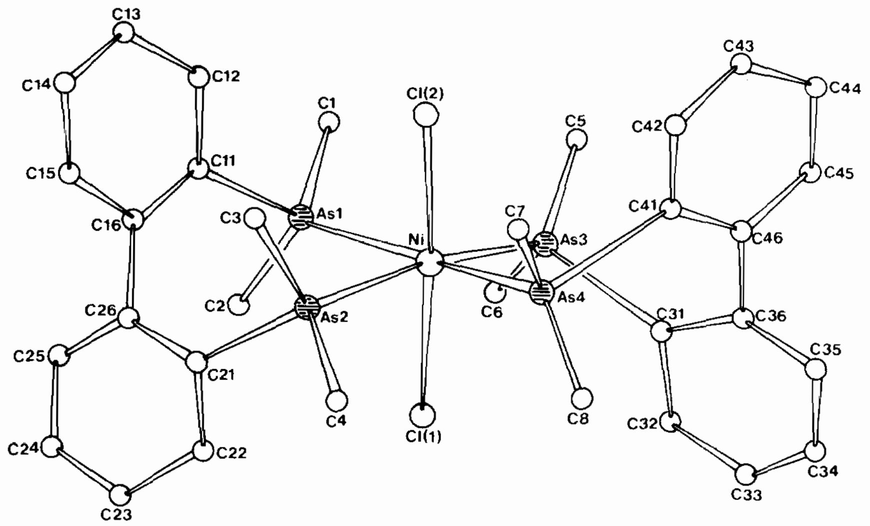
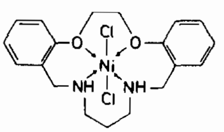


Fig. 1. Molecular structure and atom numbering scheme for [$NiCl_2(dmab)_2$]. Hydrogen atoms have been omitted for clarity.

bond distances lie close to the sum of the covalent radii of octahedral Ni^{II} (1.39 Å) and Cl (0.99 Å), [11], and are comparable with the Ni—Cl bond lengths reported [12] for the macrocyclic octahedral nickel(II) complex (2), (2.393(5), 2.395(6) Å).



(2)

Although the Ni—As distances (mean 2.507 Å) are considerably less than the sum of the covalent radii (2.57 Å), [11], they are significantly longer than the values reported for the octahedral nickel(III) complex [$NiCl_2$(*pdma*)$_2$] Cl (2.339, 2.345(3) Å), the octahedral nickel(II) complex [NiI_2(*pdma*)$_2$] (2.284, 2.302(2) Å) and the five-coordinate nickel(II) complex [$NiBr_2(Me_2As\cdot[CH_2]_3\cdot AsMe\cdot[CH_2]_3\cdot AsMe_2)$] (2.26, 2.26, 2.27 Å), [10, 5, 13]. While the elongation of the Ni—As bonds in [$NiCl_2$(*dmab*)$_2$] could be attributed to the effect of the unpaired electron in the nickel $d_{x^2-y^2}$ orbital, it could equally well reflect steric constraints within the seven-membered chelate rings. It is likely that in the free ligand the dihedral angle between the two phenyl rings is sufficiently large as to minimise the interactions between the groups *ortho* to the phenylene link. Chelation would require reduction of this dihedral angle in order to decrease the ligand-bite to a distance suitable for stable complex formation. The As—Ni—As bond angles formed by the *dmab* ligands (mean 85.90°) are similar to those in the diarsine complexes [$NiCl_2$(*pdma*)$_2$] Cl (86.8°), [NiI_2(*pdma*)$_2$] (87.5°), [10, 5], and may well represent the As—Ni—As bond angle required to optimise Ni. . .As interactions. To achieve shorter Ni—As bonds in the present complex, while still maintaining an As—Ni—As angle within the chelate rings of approximately 86°, would require reduction of the biphenyl dihedral angle below the present values of 63.1 and 60.8°. The accompanying increase in steric interaction between H15. . .H25, H35. . .H45 may however be of sufficient importance to prevent any such reduction in the Ni—As distances. The shortness of these H. . .H contacts, even in the present $NiAs_4$ geometry, suggests that such interactions are likely to be significant. Thus while the H15. . H25 distance of 2.786 Å is greater than the sum of the van der Waals radii (2.40 Å) suggested by Bondi [14], it does lie close to the value (2.90 Å) proposed by Allinger *et al.* [15]. The H35. . .H45 distance, 2.211 Å is particularly short and it is interesting to note that the associated Ni—As4 distance is significantly longer than the other three Ni—As bonds.

Bond distances and angles within the biphenyl units are as expected, although the arsenic atoms are not coplanar with their respective phenyl rings and lie out of the best least-squares planes by up to 0.056 Å. There are no significant intermolecular interactions, the most important close-contacts being between the chlorine atoms and phenyl hydrogens from neighbouring molecules (Table II).

The paramagnetic properties of [$NiCl_2$(*dmab*)$_2$] can be readily understood in terms of the distorted *trans*-octahedral environment about nickel and the analogous dibromo and diiodo compounds would be expected to have similar structures. The marked contrast in magnetic behaviour between [NiI_2(*dmab*)$_2$] and [NiI_2(*pdma*)$_2$] however is surprising, and a satisfactory explanation awaits a full crystallographic study of the comparable *dmab* complex.

Acknowledgements

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